

Standards Preparation for
Solid Sorbent Cartridges

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STANDARDS PREPARATION FOR SOLID SORBENT CARTRIDGES

by

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16. ABSTRACT An alternate technique for preparing standards of volatile organic compounds on sorbent cartridges is proposed. The system incorporates temperature controlled diffusion tubes, a multiple syringe pump and gas chromatograph. Diffusion tubes, housed in a water-jacketed chamber, maintain a constant output rate into a flowing stream of nitrogen. An equivalent portion of the gas stream is pulled across each of 13 cartridges by using a 13-position multiple syringe pump. The remainder of the gas stream is drawn through an analytical cold trap where the organics are collected and subsequently analyzed by gas chromatography. Analysis of organics on the cold trap offers a quality assurance step prior to and during cartridge loading. Analysis of traps and cartridges are highly precise. Organic vapors have been loaded onto Tenax-GC cartridges, stored for up to one month and analyzed. These results are discussed. Although all applications of this system have been to Tenax, other sorbents or collection techniques could be calibrated with this system. Results obtained with the syringe pump system will be compared to techniques for standard preparation.		
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INTRODUCTION

Volatile organic compounds are of considerable environmental interest. Emissions from mobile and stationary sources and fugitive emissions contribute potential oxidant precursors to the atmosphere, and the human health effects of volatile organic compounds and their photochemical decomposition products are of great concern. Procedures for the identification and quantification of volatile organic compounds in ambient air are still in the development stages. Several approaches for collection and analysis of specific volatile organic compounds in ambient air are possible. One common approach is to pass a known volume of air over a bed of solid sorbent packed into a cartridge. Tenax-GC is frequently used as the solid sorbent material in this technique [1]. The accumulated organic compounds are subsequently either desorbed thermally or extracted by solvents from the solid sorbent cartridge.

We have systematically studied the use of Tenax-GC for the collection and analysis of volatile organics from air. Initial concerns over the cleanliness of Tenax cartridges resulted in a suggested quantitative definition for a "clean" Tenax cartridge [2]. A cartridge holder was designed, fabricated, and tested specifically to ensure ease of use and cleanness of solid sorbents during field studies [3]. These cartridges were used to compare the sampling precision of five U.S. EPA Hi-Vol samplers equipped with dual-channel organic vapor samplers and were also used for field studies over the Houston Ship Channel area and the Ohio River Valley Basin [4,5].

During the evolution of our techniques it became apparent that a large number of multicomponent standards prepared on solid sorbent cartridges would be necessary in order to measure accurately the ambient levels of volatile organic compounds. During these studies instruments were calibrated with the

headspace vapors or solutions of pure organic compounds. These standards on sorbent cartridges were needed for routine instrument calibration, developing relative response ratios, determining sample storage lifetimes, interlaboratory comparisons, and quality assurance functions.

Methods for the preparation of standard solid sorbent cartridges fall into two categories. The first involves injecting a cartridge with a headspace sample of a pure compound or with an aliquot of a solution standard and driving off the solvent carrier. The second standards preparation system utilizes gas dilution systems in combination with diffusion or permeation tubes that deliver a gas stream of known organic concentration to the cartridge.

The objective of this study was to design and test a combined gas dilution syringe pump system for the preparation of solid sorbent cartridges loaded with known amounts of volatile organic compounds. The analysis results of cartridges loaded by this technique were compared to the results for cartridges loaded by two other techniques in use at this laboratory. Finally, the storage characteristics of the loaded standard cartridges were examined.

MATERIALS AND METHODS

The syringe pump standards preparation system incorporated three major elements in its design: the diffusion tubes and gas dilution capability, the syringe pump, and an in-line analysis system.

Diffusion tubes (Fig. 1) were chosen because of their slow constant output rate. Output rates can be approximated from published calculations [6]. For a specific compound at a constant temperature and pressure, the only controllable parameters that can change the rate of diffusion are the length and the cross-sectional area of the diffusion path. The length of the diffusion

path of commercially available tubes can be altered to achieve output rates in the desired range. The actual output rate was determined from weight loss by weighing the tubes periodically.

The diffusion tubes were housed in water-jacketed chambers (Fig. 2) and maintained at a constant temperature. The chambers were kept in a glove box for safety purposes (Fig. 3). A constant carrier gas flow and temperature were maintained across each of the chambers to maintain the constant output from each of the diffusion tubes. The mixing elements shown in Fig. 3 were constructed of glass tubing and connected with Teflon lines and fittings. A dilution chamber, constructed from a 2-l round-bottom flask with Teflon tubing, Teflon-coated stopper, and a Teflon-coated magnetic stirring bar, was fabricated to permit dilution of the organic vapor downstream from the test chamber. This dilution system has not yet been tested. For safety, the excess gas stream was vented through a furnace.

The next element in this cartridge standards preparation system was the syringe pump that we designed and fabricated. It has twelve cylinders of equal volumes, with Teflon-lined pistons all pulled at the same time and rate by a variable-speed motor. The plunger was a Teflon cylinder with two slightly raised Viton O-rings in contact with the polished stainless steel barrel. During a typical loading run each piston displaced 2.25 ml/min for 24 min. The volume withdrawn from the sample stream by each piston was drawn across each of twelve cartridges (Fig. 4) mounted to the syringe pump by quick-release levers; a thirteenth cartridge was maintained in series with the twelfth cartridge to determine if breakthrough occurred. The volume withdrawn by each piston from the sample stream was taken through a 12-position spider manifold (Fig. 5) and Teflon lines of equal length to

ensure that each cartridge was exposed to an equivalent stream. The flow through the spider manifold was maintained at approximately twice that which was drawn across the cartridges. The portion of the gas stream that was not drawn across the cartridges but drawn through the spider manifold was analyzed.

The third element of the standards preparation system was the analytical system. An analytical cold trap collected organic vapors from the spider manifold and introduced them into the gas chromatograph (GC) (Fig. 6). The GC was equipped with a 30-m SE-30 SCOT column and flame ionization detector (FID). Sample introduction was also achieved via thermal desorption or direct injection. Performance standards prior to a sample loading run included direct headspace injections, headspace injections onto Tenax cartridges, and analysis of the syringe pump vapor stream. During sample loading, a portion of the vapor stream was collected on the analytical cold trap for 6 min, flash heated to the head of the gas chromatograph for 1 min, and analyzed. After loading, blanks, breakthrough cartridges, and several cartridges were analyzed to verify the precision of loading.

We have used two other techniques to prepare standard Tenax cartridges: static dilution and flash vaporization. Pure standards (1 to 15 μ l) of volatile organic compounds were added to a sealed static dilution bottle through a Mininert valve (Fig. 7). This flask was placed in an oven and maintained at 60°C. Aliquots (50 to 200 μ l) of the agitated headspace vapor were withdrawn from the bottle and injected onto clean cartridges. Typically 100 to 800 ng of material was injected onto each cartridge. Cleanness of glassware and syringes was of utmost importance and detailed protocols were established to insure no cross-contamination.

The last technique examined here was flash vaporization. A modified injection port from a gas chromatograph was placed in line with a Tenax cartridge

and a thermal conductivity detector (Fig. 8). A solution standard was prepared in a solvent with a low breakthrough volume (e.g. methanol). An aliquot of the solution standard was injected into the heated GC injection port, volatilized, and deposited onto the Tenax cartridge, which was maintained at ambient temperature. The cartridge remained in the gas stream until the methanol was swept away, as indicated by the thermal conductivity detector.

Quantitative analyses were by thermal desorption GC, and confirmational analysis was provided by GC/MS. All cartridges were constructed and prepared according to specifications described elsewhere [4].

Little data were available on the effects of storing Tenax cartridge standards or samples. Because most of the applications for Tenax standards require that the standards be stored for some period of time, we also investigated the stability of volatile organics on Tenax. Twenty-eight cartridges were loaded by the syringe pump technique with five compounds: perfluorobenzene, benzene, chloroform, trichloroethylene, and chlorobenzene. The cartridges were stored with blanks in culture tubes and sealed paint cans at room temperature. Randomly selected cartridges in addition to blanks and external standards were analyzed in groups of four over a 28-day period.

RESULTS AND DISCUSSION

The output rate of the diffusion tubes was of great importance during these studies. Without a constant effusion rate, it would be impossible to prepare precisely loaded cartridges. Table I shows typical output rates for diffusion tubes containing several of the volatile organic compounds studied over the last several years. Minor fluctuations encountered since 1978 are most likely due to differences in environmental conditions, such as room pressure changes, or due to errors associated with the weighing procedures. Indeed,

analysis results discussed later suggest that output rates are even more constant than indicated by the weight loss determined by periodic weighings. The effect of the absolute error associated with weighing on precision balances was magnified when the weight loss was small, i.e., low output rates (< 100 ng/min). At one point during the study, helium was substituted for nitrogen as the carrier gas and the output rates increased by nearly a factor of three, as one would predict. During normal usage, the diffusion tubes would require refilling every two to three years.

As part of the protocol for determining the instrumental precision, performance standards were analyzed daily, generally by direct injection of some solution standard. However, this did not always reveal all the problems with the analytical system. Some leaks in the six-port valve and other portions of the thermal desorption system were not revealed by this technique. Therefore, as part of the protocol, an aliquot of the headspace of perfluorobenzene (PFB) was injected directly into the gas chromatograph (GC); a second was injected onto the cold trap and subsequently flash-heated to drive the accumulated materials onto the GC column; and a third was injected onto a Tenax cartridge, thermally desorbed onto the cold trap and then flash-heated into the GC (See Fig. 6). Headspace concentrations of PFB were determined from published vapor pressures [7].

An equivalent response for all three types of sample introduction was expected and required by the protocol before proceeding with further analysis or standard cartridge preparation. For other compounds, a lesser degree of efficiency was obtained for thermal desorption from Tenax. Table II presents the results for eight absolute response determinations for PFB and 4-chlorotoluene by the three sample introduction types and shows that within experimental error direct GC injections and injections onto the cold trap with subsequent GC

analysis yielded similar recovery efficiencies. All measurements were for 2- μ l injections from 5- μ l syringes. PFB injected onto and thermally desorbed from Tenax cartridges also indicates 100% recovery, but only approximately 25% of the 4-chlorotoluene was recovered from the Tenax.

We have used six different thermal desorption units as sample introduction systems for GC and GC/MS (three commercial and three built at NSI machine shops) and found that there is some variability in desorption efficiencies. When collecting and analyzing environmental samples, it will be most important for high accuracy to determine the relative desorption efficiencies for the compounds of interest from the solid sorbent used and not just the relative instrumental response ratios from solution standards.

Estimates of the loading precision for eight compounds prepared on Tenax cartridges with the syringe pump system are shown in Table III. The cold trap observations are for those samples collected during a standard cartridge loading run from the organic vapor-laden carrier gas stream on the liquid nitrogen cold trap. Typically the organic vapor-laden stream is sampled at 25 ml/min for 24 min. At the end of the standard cartridge loading run, the liquid nitrogen Dewar is lowered and the trap is flash-heated. This sample is a subsample of the diluted organic vapor stream that is pulled across the twelve Tenax cartridges by the syringe pump. Concentrations for individual compounds in the carrier gas stream range from 2 to 10 ng/ml. Analysis results of cold trapping runs were very precise, with standard deviations ranging from 0.4 to 1.3%. These results were substantiated with subsequent measurements and, because of the excellent precision, cold trapping runs were used as an additional quality assurance step to the PFB headspace injections for the analytical system performance. Analytical results for multiple, daily PFB headspace injections into Tenax cartridges and subsequent thermal desorption

and analysis with five GC and three GC/MS systems over the last two years suggested that an overall average variation of ± 6 to 8% was the best to be achieved by an experienced technician.

With each cold trapping run, ten Tenax cartridges loaded with standards were analyzed by thermal desorption GC-FID. The relative standard deviations ranged from ± 5 to 10%, certainly an acceptable level for ambient measurements of volatile organic compounds. With proper preparation, at most 36 standard cartridges could be prepared in a normal working day. The difference in variability between the analytical precision for the cartridges and the cold trap is most likely due to the error associated with the thermal desorption of Tenax cartridges: the precision of direct GC injections of PFB headspace vapor was improved from the values presented in Table II to about $\pm 1.0\%$ by experienced staff, while headspace injections of PFB onto Tenax cartridges with subsequent thermal desorption yielded precision no better than ± 6 to 8%.

This system can be used for an indefinite period of time and requires little in the way of maintenance. If large numbers of standard cartridges are needed, this system will continue to produce standard cartridges for weeks or months. However, this system requires a skilled technician who can recognize problems with the various elements of the system, diffusion tubes, syringe pump and gas chromatograph. The most frequently encountered problems were leaks either in the carrier gas lines, the six-port valve, or the injection system.

The static dilution and flash vaporization techniques for the preparation of standard solid sorbent cartridges of volatile organic compounds are relatively inexpensive, easy to prepare, and simple to use. These two techniques for the preparation of solid sorbent cartridges have been recently adopted by our laboratory. The results for repetitive analysis are shown in Table IV. For

this study the chlorobenzene and ethylbenzene peaks were not resolved and have been reported as a single peak. Since quantitative analyses were by GC-FID, the quantitation of these two compounds individually was not possible. The two peaks could be resolved by using the mass chromatogram technique, choosing the diagnostic ion for each of the species. Once again the precision of analysis for the standard cartridges is in an acceptable range for ambient measurements. From our experience, headspace injections require some practice before good precision will be obtained. Similarly, the precision of desorptions of volatile organic compounds from Tenax, whether loaded by syringe pump or headspace injection, seldom has been better than about $\pm 5\%$.

Typical chromatograms generated by these two techniques are depicted in Fig. 9. The standard Tenax cartridges prepared by the flash vaporization technique contain some residual methanol, which could interfere with the analysis of some compounds of interest.

The static dilution bottle was preferable to the syringe pump system for the preparation of a small number of standard cartridges. Tens of cartridges can be produced daily. After several days of use it is necessary to recycle the bottle, which is rather labor-intensive. Although the flash vaporization technique was used here for volatile organic compounds for comparison purposes, its real advantage comes from allowing a precise injection of a solution standard of compounds of lesser volatility than those used in diffusion tubes or static dilution bottles. The flash vaporization system produces fewer cartridges per day (30 to 60 min per cartridge) but has no recycling limitations.

As mentioned previously, there are few applications for standard solid sorbent cartridges which permit them to be prepared fresh daily. The analysis results for 28 standard cartridges (analyzed in groups of four per day) loaded with five compounds by the syringe pump technique and stored for 28 days at

room temperature are shown in Table V. Cartridges were selected and analyzed randomly on days 0, 3, 5, 10, 14, 20 and 28. The concentrations are reported as nanogram equivalents of PFB; that is, for this study the absolute responses were determined and the relative response ratios were not.

On the basis of correlation coefficients computed by linear regression techniques, three compounds showed no discernible trend in recovery as a function of storage. Trichloroethylene results support a weak negative correlation, while the results for the chlorobenzene indicate a decided negative correlation. These results suggest that Tenax sample storage may result in losses of species with lower volatilities. Some sort of irreversible adsorption phenomenon may account for this behavior. However, the reproducibility of the analyses appears to remain good over the 28 days (Table V). The precision of these analyses suggests that these losses are real.

From these results it is obvious that standard solid sorbent cartridges prepared with the volatile organic species which are to be quantitated in field studies should be prepared at appropriate concentrations and stored for similar lengths of time to determine real sample losses due to storage time. Although all results discussed here were for Tenax-GC as the solid sorbent, any solid sorbent may be subjected to these standard preparation procedures.

A general comment is necessary here on the problems encountered with the environments of laboratories and the effects on the preparation of low concentration Tenax cartridge standards of volatile organic compounds. Hubbard et al. [2] pointed out that a clean Tenax cartridge placed in a culture tube with a Teflon-lined screw cap and left on a laboratory bench accumulates significant levels of volatile organic compound in several days. A constant sense of awareness must be maintained to avoid contamination by normal laboratory solvents. In addition, one must always be aware of well-intentioned facilities

support personnel who paint, use aerosol lubricants, spray for insects, use organic solvents as cleaners, etc. Similarly, photocopiers requiring the use of volatile organic solvents, leaking freezers and air conditioning systems contributing freons, and the use of aerosols to treat plants by office personnel all add to the volatile organic background of the facility. Multiple quantitative blanks are required for all standards preparation and field studies in order to accurately report ambient levels of volatile organic compounds.

CONCLUSIONS

A standard solid sorbent cartridge system incorporating a syringe pump, diffusion tubes, a gas dilution system, and an in-line analysis system has been designed, built, and tested. The diffusion tubes used have maintained a constant output as determined by periodic weighings. Precisely loaded Tenax cartridges (± 5 to 10%) have been prepared by this system and compared to two other standard cartridge preparation techniques: static dilution bottles and flash vaporization. All three techniques produce precisely loaded Tenax cartridges for the compounds examined. The syringe pump system is the most expensive and time-consuming to get into routine operation but can produce a significantly greater number of standard cartridges than the other techniques. The static dilution bottle and flash vaporization methods produce precisely loaded cartridges and are inexpensive and simple to use. The static dilution bottle will also produce a large number of cartridges over a short period of time (several days) before recycling of the glassware would be necessary. Flash vaporization is ideally suited for compounds whose volatilities prevent them from being used in diffusion tubes or static dilution bottles.

Standard Tenax cartridges prepared by the syringe pump technique and analyzed over a 28-day period suggest that the recovery efficiencies of the species with lower volatilities may be reduced with storage time.

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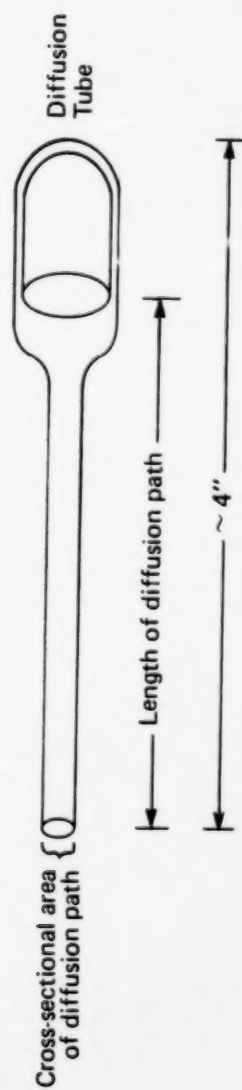
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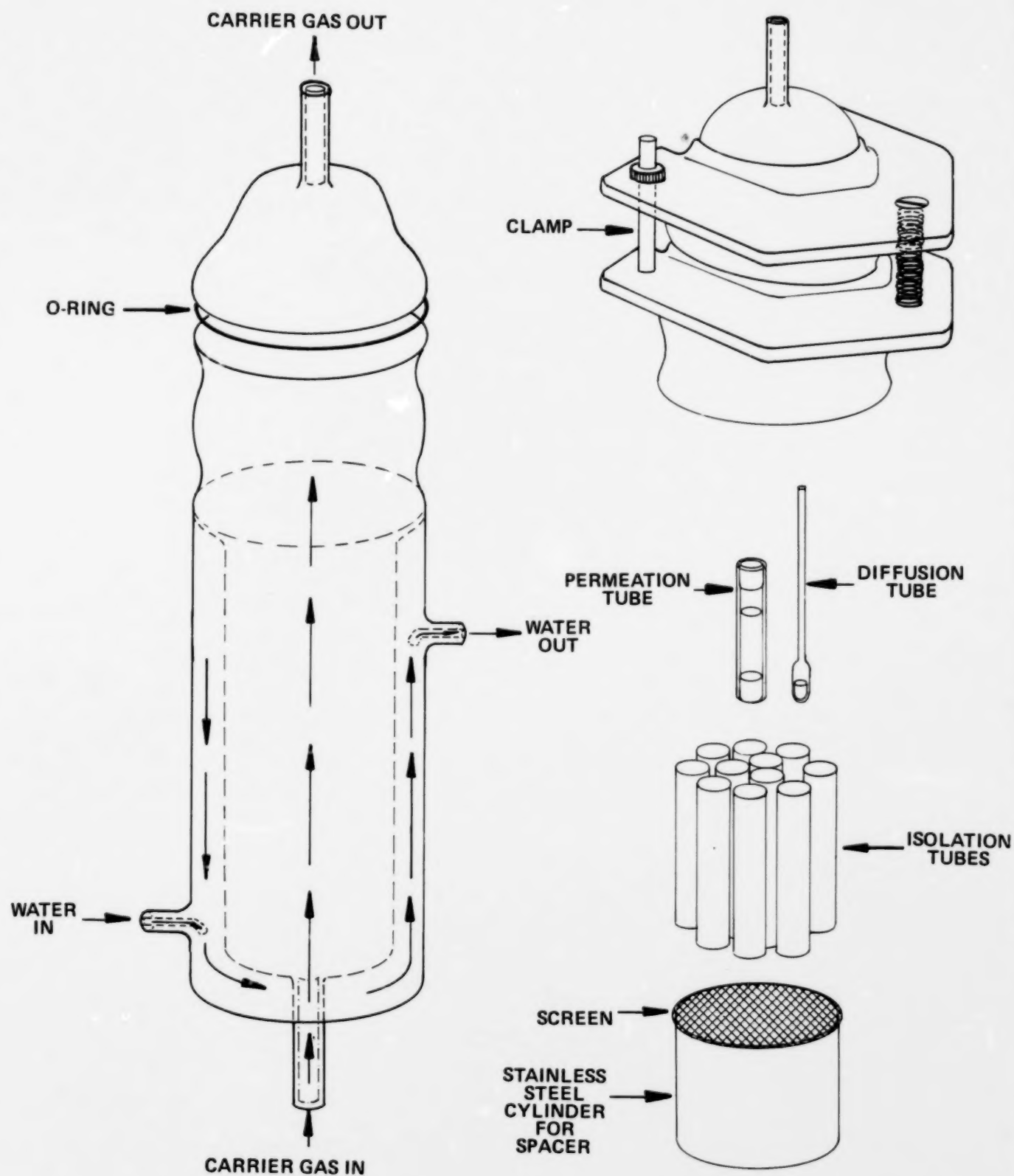
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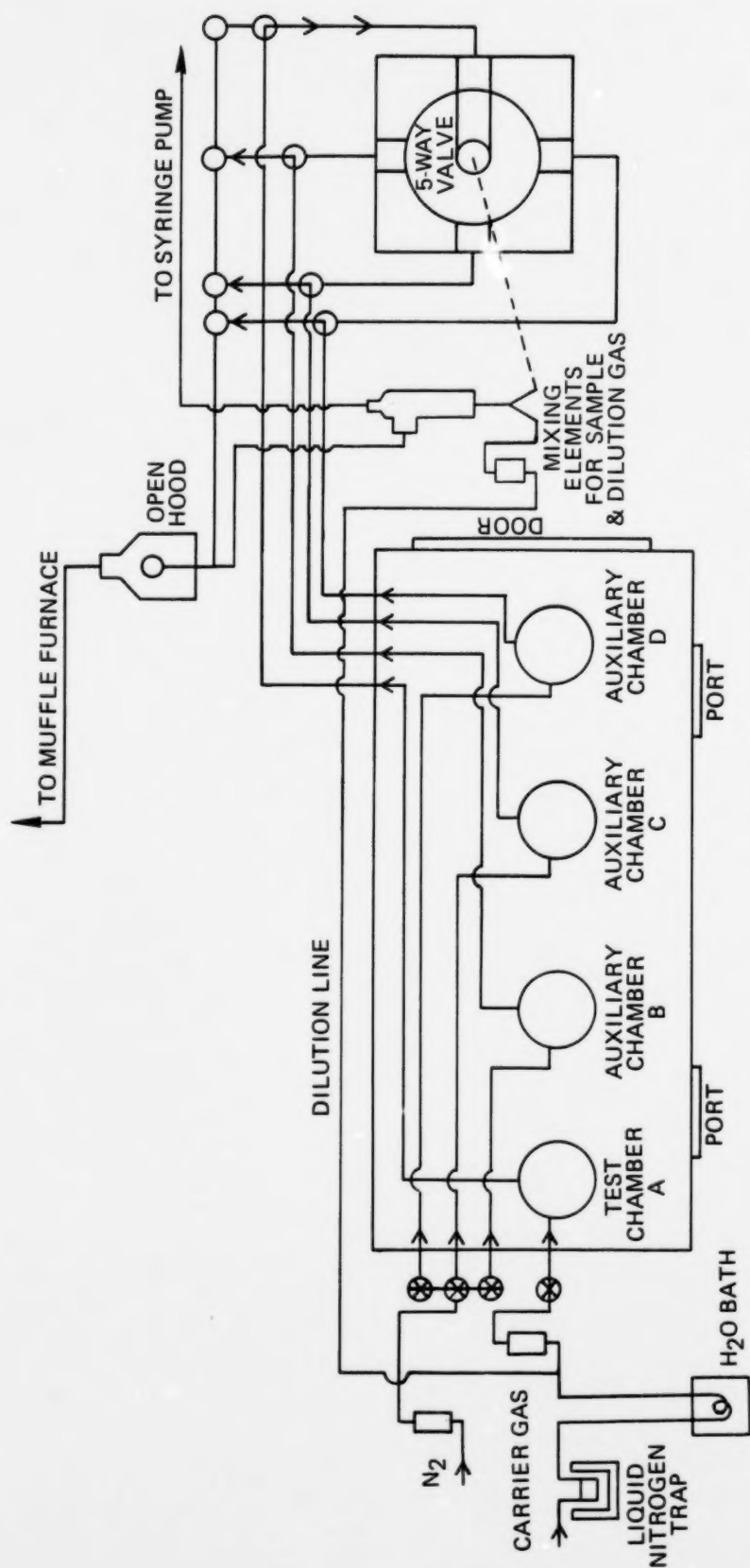
Figure Legends

- Figure 1. Diffusion tube used in standards preparation. The tube was constructed of glass with a precision bore capillary extending from the reservoir.
- Figure 2. Water-jacketed chamber for diffusion tubes. The chamber was fabricated from a 3 1/2-in glass #75 O-ring ball joint and sealed with a Thomas clamp. The glass diffusion tubes within the chamber rest on a stainless steel screen above a stainless steel cylinder to allow an even air flow through the glass isolation tubes.
- Figure 3. Gas dilution system.
- Figure 4. Syringe pump.
- Figure 5. Syringe pump sample path.
- Figure 6. Six-port valve. The analytical cold trap is 1/16-in nickel tubing (approximately 30 cm long) fitted with a 6-port high-temperature Valco valve (ACV-6-HTA) with a heater block, 6-in standoff, and an air activator. A Schroder Gold Medallion miniature cylinder is used for pneumatic air lift over a 6 1/2-in Pope Dewar flask. The helium flow is monitored by a Brooks Model 5810-1K1D4A mass flowmeter (range 0-10 SCCM) and the flow through the trap by a Brooks Model 5810-B1C3D4A mass flowmeter (range 0-50 SCCM).
- Figure 7. Static dilution bottle. A 2-l round-bottom flask is fitted to receive a 20-mm screw cap Mininert valve. A 1 1/2-in Teflon-coated stirring bar and 3-mm glass beads are used to agitate the contents.
- Figure 8. Flash vaporization system. This system is composed of an insulated gas chromatograph heater block (Tracor GC) with carrier gas line, cartridge heater, and thermocouple and is fitted with inlet line, septum and septum nut, 1/8" stainless steel exit line, and Nupro fine metering valve. The 8 x 1.5 cm stainless steel cylinder is joined to the Tenax tube with stainless steel swage fittings.

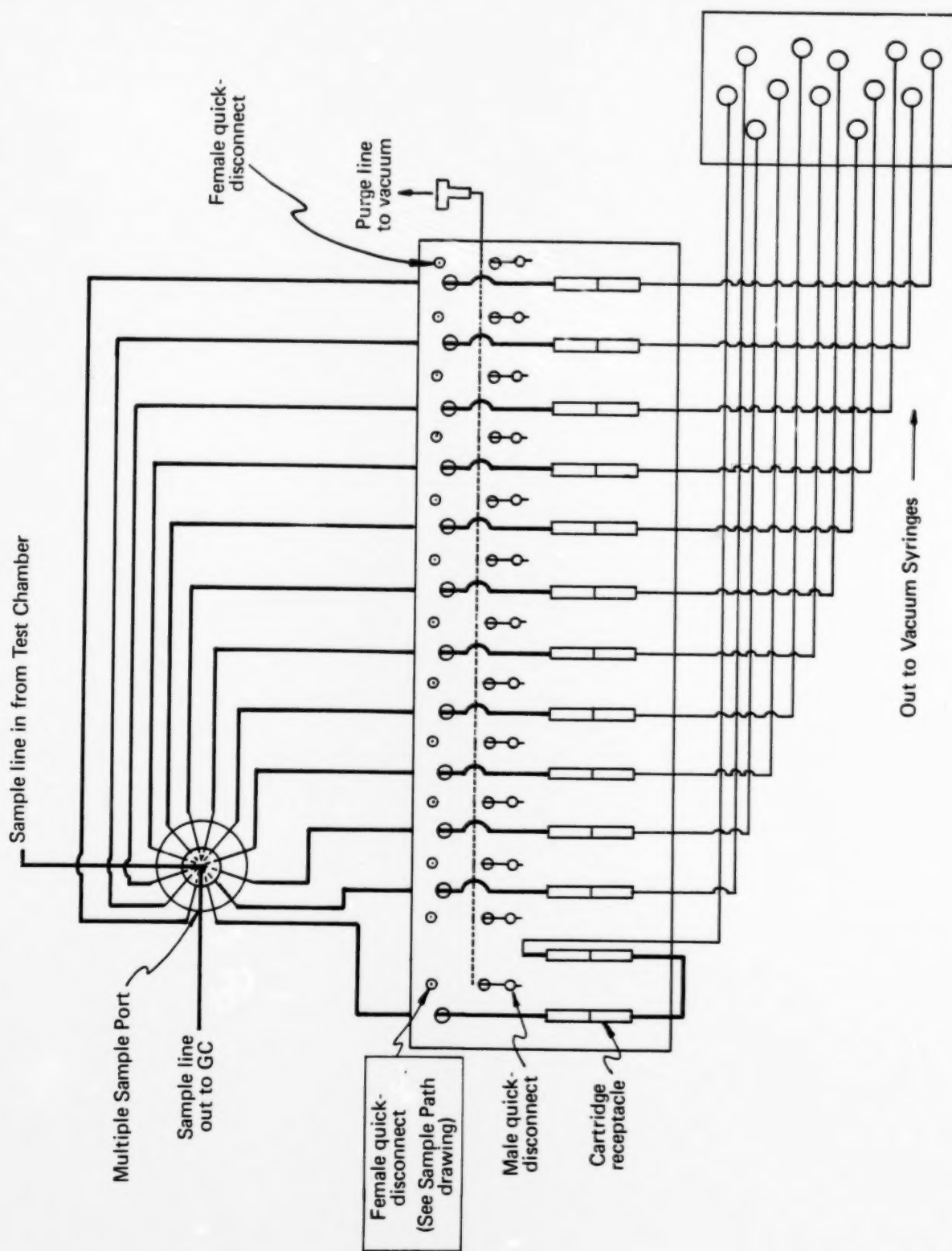
Figure 9. Comparison of chromatograms resulting from analysis of standard cartridges prepared by static dilution and flash vaporization. The GC was heated from 30°C to 130°C at 4°C/min with a helium flow rate of 2.5 ml/min through a 24.5-m SP 2250 SCOT column. Sample sizes ranged from 100-200 ng (low levels) to 600-700 ng (high levels). Because the two chromatograms were generated from different test atmospheres, no quantitative comparisons can be made for individual peak heights.

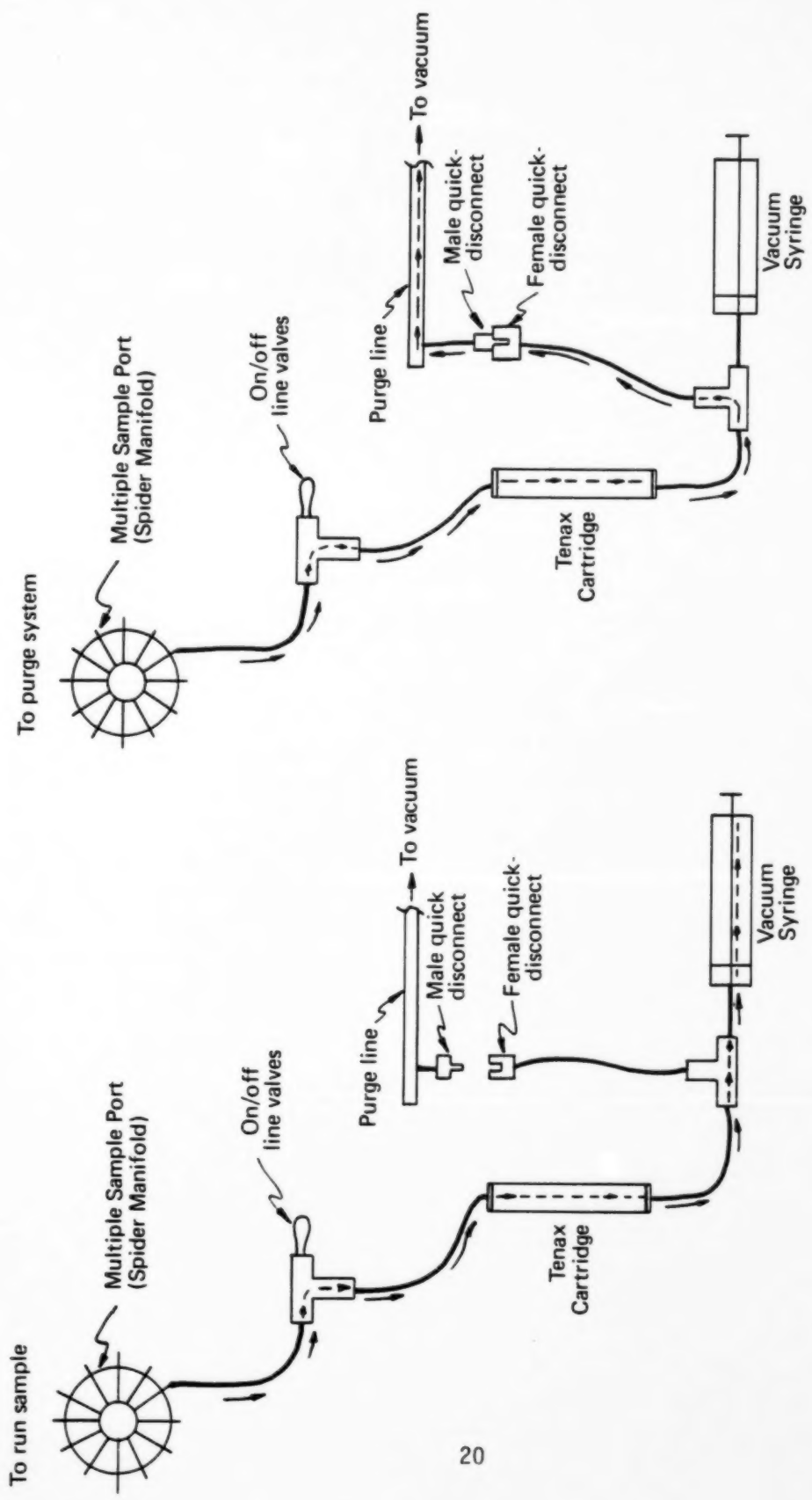


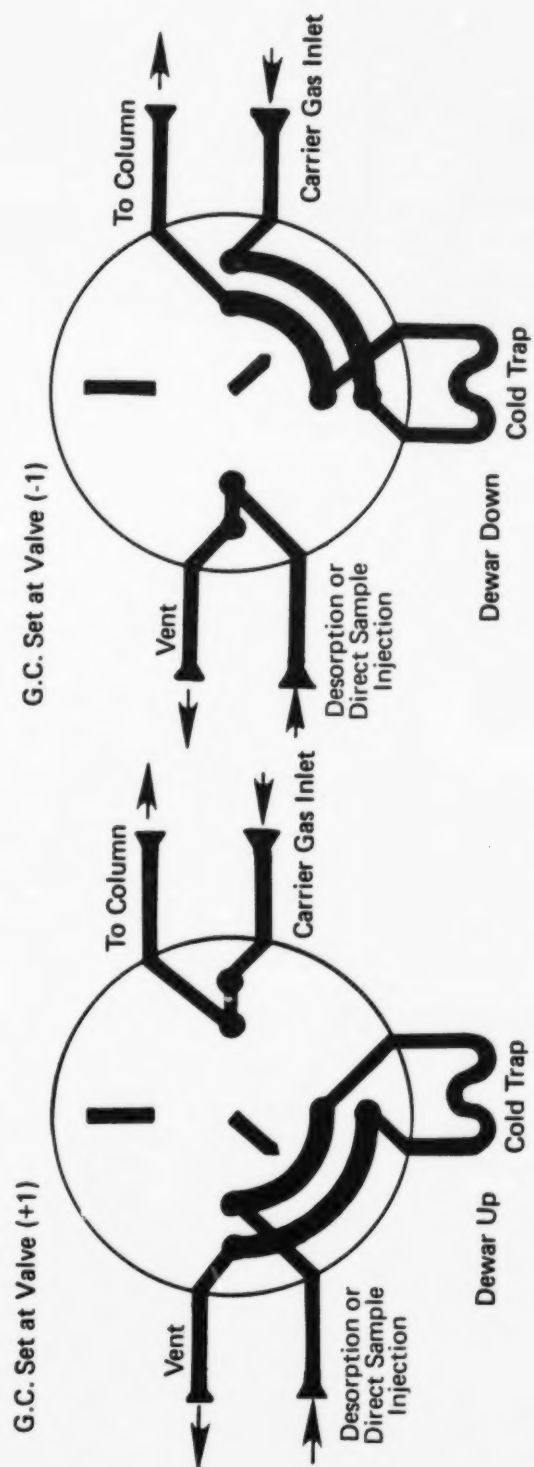




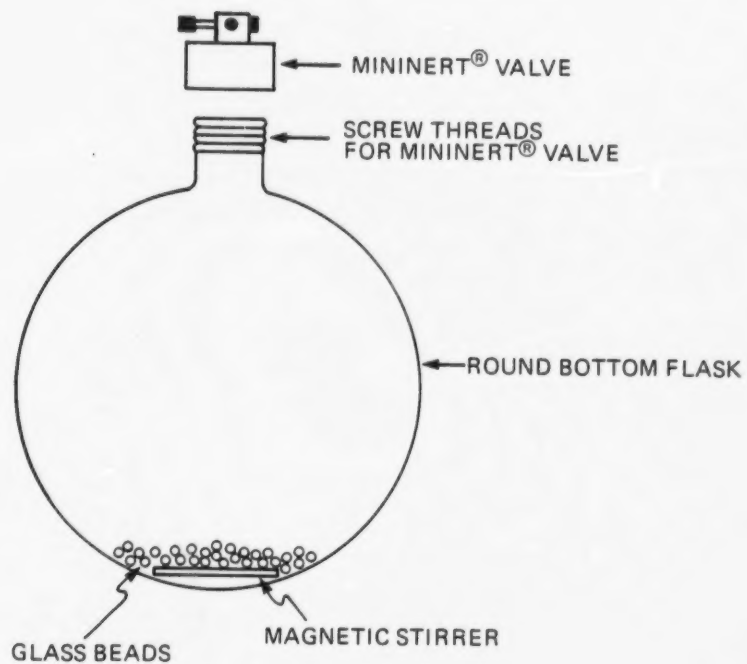
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- ⌈ — ROTAMETER FLOW CONTROLLER

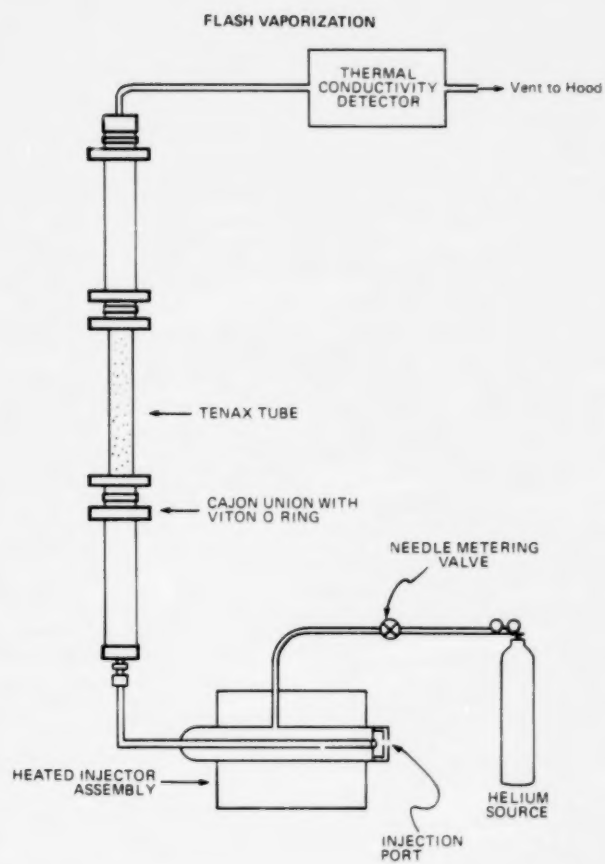




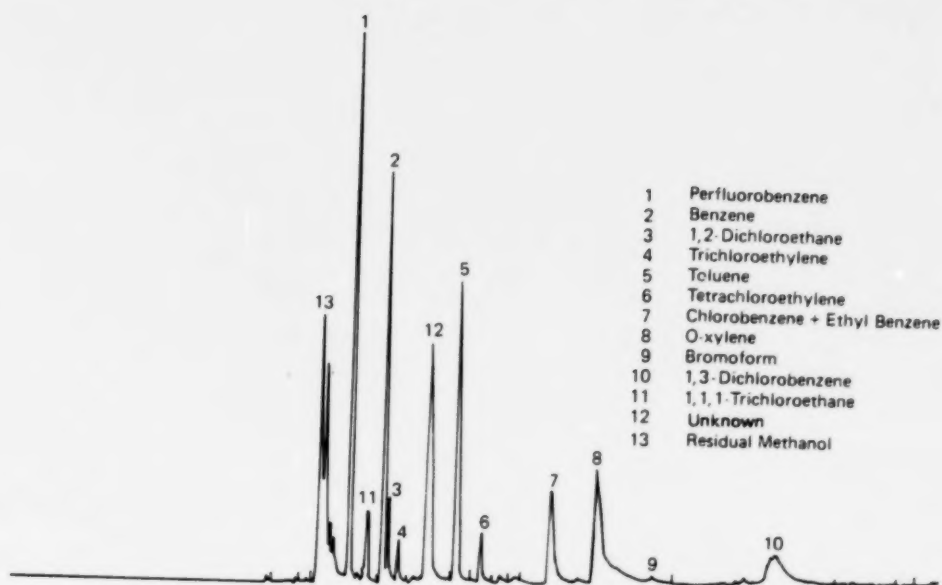


STATIC DILUTION





FLASH VAPORIZATION LOADING



STATIC DILUTION LOADING

